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COLLINGWOOD HARBOUR

REMEDIAL ACTION PLAN

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MUSSEL BIOMONITORING

1990

DATA REPORT

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Remedial Action Plan
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PREFACE

This report has been prepared under the auspices of the Canada-Ontario Great Lakes Remedial Action Plan Program.

Financial support for the investigation was provided by Environment Ontario.

The report is the fourth in a series of technical investigations conducted insupport of the Collingwood Harbour Remedial Action Plan and was written by G. Krantzberg, Collingwood Harbour RAP Coordinator, Environment Ontario, Water Resources Branch.

The report presents the findings and conclusions of the author and does not necessarily represent the view or polices of the sponsoring agency.

FOREWORD

Since designation of Collingwood Harbour as an Area of Concern in 1977, the Collingwood Harbour Remedial Action Plan (RAP) has been working towards ways of addressing and correcting the harbour's environmental problems. The fundamental goal of the Collingwood Harbour RAP continues to be the improvement and protection of the quality of Collingwood Harbour's waters. In consultation with the community, the Public Advisory Committee (PAC) has identified goals and uses for the harbour, and proposed to the RAP Team a strategy combining the preferred remedial options.

Environmental conditions that detract from the goals and uses are the primary concern of the RAP. While water quality has improved substantially over the past decade, several problems still remain. Chief among these is nuisance algal growth, caused by excessive levels of phosphorus and other nutrients in the water. Sediment contamination from historical industrial activities is a potential concern. Bioassessment of Collingwood Harbour in 1986, 1988 and 1989 included *in situ* algae, fish, mollusc, and benthic invertebrate studies, and laboratory studies on fish and benthic invertebrates. The current study reexamined the ability of freshwater mussels to accumulate trace metals and trace organic contaminants when placed in the harbour and the harbour tributaries. The emphasis was on determining whether chlorinated hydrocarbons were present in sufficient concentrations to impair aquatic biota.

The findings of this report will be included in the Stage 2 document, in the evaluation of preferred options. A concerned and actively involved public is vital to the RAP process, and to the future of Collingwood Harbour. The environment, and the choices that are made to preserve and restore it, are community concerns. If the preferred remedial actions are going to be successful, it will require the effort, resources and dedication of a well informed community.

ACKNOWLEDGEMENTS

I thank W. Page, G. Hobson and the field crew for their efforts in mussel deployment and retrieval. I particularly thank P. Kauss, D. Boyd, other members of the Water Resources Branch and the RAP Steering Committee for their valuable comments in review of this report. The Collingwood Harbour RAP Team and PAC also provided insightful comments on the development of this project and the data report.

ABSTRACT

Mussels can be used to monitor whether contaminants in aquatic ecosystems are available to the animals inhabiting that ecosystem, and to measure the potential for those contaminants to enter the food web. The objective of the present investigation was to determine whether there is a need to develop remedial options for sediment in the southwestern portion of the harbour, in the vicinity of the old Imperial Oil wharf.

Mussels were submerged in Collingwood Harbour and its tributaries for three weeks during the summer of 1990. Mussels were retrieved, shucked, and wrapped in hexane-rinsed aluminum foil or "whirlpak" bags for trace organic and inorganic chemical analyses, respectively. Sediment was collected concurrent with mussel retrieval.

With the exception of zinc in two of the tributaries, metal and trace organic contamination is not apparent in exposed mussels or sediment of the creek, canals or harbour. While of potential concern, it should be noted that high concentrations of zinc are not found in harbour sediment and zinc is marginally elevated only in mussels in several of the inflows. In addition, due to the intermittent nature of flow in the tributaries, these streams provide poor habitat for benthos and fish. Consequently, exposure of biota in these habitats is limited. Other metals which were found at concentrations above the provincial sediment guidelines approach background concentrations for the area.

Data from the present study support previous findings that trace organic contaminants, including PAHs, are not an environmental concern for Collingwood Harbour. No PAHs, PCBs or pesticides were detected in mussels or sediment, with the exception of low concentrations of some PAHs in sediment from Oak St. Canal. Concentrations in Oak Street Canal represent concentrations typical of relatively uncontaminated sites in urban watersheds.

INTRODUCTION

Mussels can be used to monitor whether contaminants in aquatic ecosystems are available to the animals inhabiting that ecosystem, and to measure the potential for those contaminants to enter the food web. The freshwater mussel Elliptio complanata is suitable for monitoring the bioavailability of prgampcj;prodes amd polyaromatic hydrocarbons (PAH) (Heit et al. 1980, Kauss and Hamdy 1985, 1991, Innes et al. 1987). Freshwater and estuarine mussels are also well known for their ability to accumulate metals and have been used extensively for evaluating trace metal contamination in aquatic environments (Smith et al. 1975, Lakshmanan and Nambisan 1989, Pugsley et al 1988, Phillips 1979, Chu et al. 1990).

In 1989, no data existed on the presence or biological availability of potentially toxic polyaromatic hydrocarbons (PAH) in Collingwood Harbour in the vicinity of the defunct Imperial Oil wharf location or of contaminants that may be associated with the Goodyear outfall in Black Ash Creek. If any oil residues exist, they could contain PAH residues.

In 1988, a single sediment sample split revealed high oil and grease concentrations, although the companion split had very low oil and grease concentrations (Krantzberg et al. 1989). This anomaly may be due to sample preparation and analytical uncertainty, nevertheless, confirmation that PAH residues are not excessive was required.

In 1988, the young-of-the-year spottail shiner program submitted a single sample for PAH analysis. This program samples the young-of-the-year shiners throughout the Great Lakes to identify whether contaminants are biologically available. Results obtained for this sample in 1990 indicated that tissue residues in shiners were elevated (Suns et al. 1991). This result is to be confirmed when the results of the 1990 survey on a larger sample size are received, and will complement the mussel biomonitoring study described herein.

The objective of the present investigation was to determine whether there is a need to

develop remedial options for sediment in the southwestern portion of the harbour, in the vicinity of the old Imperial Oil wharf by:

- deploying caged mussels as biomonitors of organic and inorganic contaminants

- comparing tissue residues in mussels with sediment chemistry and with tissue residues in control organisms

PROJECT DESCRIPTION:

Three stations in the harbour were selected to overlap with the shiner collections, as well as to focus on potentially contaminated sites based on historical activities in the harbour. Additional locations in the creek and canals were also sampled (Figure 1).

During the summer of 1980, triplicate cages containing five mussels each were submerged in the harbour at stations 21, 32 and 25, at the tributary stations 13, 14, 15 and at the Goodyear effluent confluence with Black Ash Creek. After three weeks mussels were retrieved, shucked, and three samples, each of four animals, frozen on dry ice in the field and submitted to the Rexdale MOE laboratory. The remaining three animals were included in the cages as a precaution in the event of mortality.

For each sample of four mussels, two animals were individually wrapped in hexane-rinsed aluminum foil, and two animals were individually bagged in plasic "whirlpak" bags for trace organic and inorganic chemical analyses, respectively. Three samples of 4 Balsam Lake control animals were also submitted to the laboratory.

Duplicate sediment samples were collected concurrent with mussel retrieval. For the harbour locations, sediment was sampled by Ponar grab, and the top two to three cm were removed using plastic spoons and placed in plastic PET and amber glass sample

jars for metal and organic analyses, respectively. At the tributaries, sediment was retrieved using hand held stainless steel coring devices inserted to a depth of three cm. Cores were pooled and homogenized in order to acquire sufficient material for analysis. All samples were placed in ice-filled coolers, and transported to the laboratory for analyses.

ANALYTICAL METHODS

All chemical analyses followed the Ontario Ministry of the Environment protocols detailed in "Outlines of Analytical Methods" (OME, 1983). Following this procedure, > 2.5 gm of organisms were digested in nitric:perchloric acid (5ml:2ml) at room temperature for several hours, at 120 °C for two hours followed by 170 °C for 4 hr. Digestion tubes were allowed to cool, sample volume brought to 25 ml with double distilled water, and analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy or by Flameless Atomic Absorption Spectrophotometry.

Quality control was monitored by the inclusion of replicates and routine blanks, spikes and standard solutions. Depending upon the final test organism biomass available for analysis, duplicate or triplicate analyses were performed. Blank and standard solutions were analyzed once per run of 15 to 20 samples.

Total organic carbon was determined by measuring both total carbon and percent inorganic carbon and then subtracting to obtain total carbon. Total carbon was analyzed using the Leco CR-12 Carbon Analyzer to combust the sample at 1370 °C to remove carbonates. Carbonate carbon was measured as CO_2 evolved by reaction of carbonate with 2N HCl swept by purified air through a KI scrubber into the cathode compartment of a coulometer.

Particle size was evaluated using the standard Ontario Ministry of the Environment protocol, employing a Leeds and Northrup Laser Diffractor. Samples were air dried,

disaggregated by hand with a mortar and pestle, and the >2mm size fraction discarded. Slurries containing Calgon (sodium hexametaphosphate) as a dispersant were introduced into the instrument and laser diffraction was measured. This technique provides information on particle sizes ranging from 0.17 um to 1000 um. The greater than 1000 um fraction was quantified, but not further subdivided. Comparison of this method with the pipette method demonstrates that the aggregations of fine organic particles are better dispersed and particle size distributions more accurately reflect sediment characteristics using the laser diffractor.

For PCBs and organochlorines, tissues were digested in concentrated HCl and then extracted with 25% dichloromethane in hexane (v/v). Powdered $NaHCO_3$ was added to the extract to neutralize the sample. The extract was dried over Na_2SO_4 and volumetrically diluted to 100 mL in hexane. Aliquots were submitted for cleanup using dry Florisil 100-200 mesh, dry pack. Extracts were analyzed by electron capture (Ni^{63})-gas chromatography using a Hewlett Packard gas chromatograph.

Tissues for PAH analyses were digested as above, with the addition of 0.5 mL of d_{10} anthracene following dichloromethane addition. The samples were then subjected to vortex evaporation to 1 mL and to final dryness using nitrogen. 2.5 mL of dichloromethane-cyclohexane were added to the residue, and the solutions were cleaned up using the SEHPLC system. The vortex-evaporated PAH fractions were resuspended in 0.5 mL isooctane and analyzed by a Hewlett-Packard 5790 capillary gas chromatograph/mass selective detector with a HP ChemStation Data Station. d_{12} chrysene was used as the internal standard.

RESULTS

The results of mussel and sediment collections and analyses are described by station. The full data sets are found in Table 1 through 3.

OAK STREET CANAL (14) elevated zinc in mussels, very low concentrations of all other metals in mussels and sediment. No detectable pesticides in mussels and sediment, traces of some PAH in sediment.

HICKORY STREET CANAL (15) elevated zinc in sediment, very low concentrations of all other metals; organic contaminants in sediment at detection limit and below detection in mussels.

BLACK ASH CREEK (13) low concentrations of all metals in sediment and mussels; no detectable organic contaminants in sediment and mussels.

GOODYEAR OUTFALL (11) elevated zinc in sediment and mussels, low concentrations of all other metals and no detectable organic contaminants in sediment and mussels.

CENTRE HARBOUR (25) low concentrations of all metals in sediment and mussels; no detectable organic contaminants in sediment and mussels.

EAST HARBOUR BY SHIPYARDS (21) low concentrations of all metals in sediment and

mussels; organic contaminants in sediment at detection limit and below detection in mussels

STP PRECHLORINATION (3) low concentrations of all metals in sediment and mussels; no detectable organic contaminants in sediment and mussels.

WEST HARBOUR BY DEFUNCT IMPERIAL OIL WHARF, BLACK ASH CREEK MOUTH (32) low concentrations of all metals in sediment and mussels; no detectable organic contaminants in sediment and mussels

BALSAM LAKE CONTROLS

DISCUSSION and CONCLUSIONS

With the exception of zinc in two of the tributaries, no metal or trace organic contamination of exposed mussels or sediment is apparent in the creek, canals or harbour. Other metals that are above the provincial sediment guideline approach background concentrations for the area with the exception of lead in Hickory Street Canal (Krantzberg 1991).

Zinc is an essential element and not highly toxic, except at extremely elevated concentrations. For example, Krantzberg and Boyd (1991) demonstrated no mortality, and growth comparable to controls, when mayfly nymphs and fathead minnows were exposed to sediment from Hamilton Harbour containing in excess of 2000 $ug.g^{-1}$. Many organisms, including freshwater mussels, are known to be capable of regulating their tissue concentration of Zn (Langston and Zhou 1986, Phillips 1985, Chu et al. 1990, Krantzberg and Stokes 1989). The poor relationship found between Zn in mussels and sediment (Figure 2) suggests that:

a) mussels are able to modify their tissue concentrations of zinc through metabolic pathways

b) the biological availability of zinc varies widely among stations and bulk sediment chemistry is a poor indicator of zinc that is available for uptake and retention by mussels

The land adjacent to the tributaries at the southern end of the harbour perimeter is a filled landfill site. Among the sources of waste in the landfill are Goodyear Rubber, Harding Carpets and LOF Glass (P. Dunbar, pers. comm.) It is possible that zinc in the tributaries is associated with zinc stearate used in processing rubber, which has migrated out of the landfill site. While of potential concern, it should be noted that high concentrations of zinc are not found within the harbour and zinc is marginally elevated only in mussels in several of the inflows. In addition, due to the intermittent nature of flow in the tributaries, these streams provide poor habitat for benthos (Krantzberg, per. obs.) and fish (A. Smith, MNR, pers. comm.). Consequently, exposure of biota in these habitats is limited.

Despite the elevated lead concentrations in Hickory Street Canal, tissue residues in mussels are comparable to controls. It is possible that with longer exposure times, lead concentrations in mussels would increase, although the abiity of mussels to accumulate metals rapidly has been shown (Lakshmanan and Nambisan 1989). This canal flows intermittently, and lead concentrations are at or below the detection limit during high flow conditions associated with storm events (RAP unpubl. data).

Data from the present study support previous findings that trace organic contaminants, including PAHs, are not an environmental concern for Collingwood Harbour. No PAHs, PCBs or pesticides were detected in mussels or sediment, with the exception of low concentrations of some PAHs in sediment from Oak St. Canal. Substances such as pyrene and chrysene are found, in part, in petroleum products and are generated as a result of incomplete combustion of fossil fuels (USEPA, 1977). The draft Provincial Sediment Guidelines (Persaud et al. 1991) have proposed that the tentative "Lowest

Effects Level" (LEL) for total PAHs be 2 $\mu g.g^{-1}$ dry weight. The LEL corresponds to the guideline value for the open water disposal of dredged sediment. Alden and Butt (1987) found no effects on mortality and respiration rate for grass shrimp exposed to sediment containing total PAH concentrations of 2.9 to 15.5 $ug.g^{-1}$ and considered these materials suitable for open water disposal. Draft PAH goals for the Netherlands cite a standard value of 0.5 $\mu g.g^{-1}$ for each individual PAH, which is equivalent to 8 $\mu g.g^{-1}$ total PAH for the 16 compounds Environment Ontario measure (van Veen and Stortelder, 1988). Using four separate approaches to developing sediment quality criteria, Chapman et al. (1987) derived values for PAHs at, or below which, biological effects have been shown to be minimal for PAHs. These ranged from 2.0 to 12.0 $\mu g.g^{-1}$. Concentrations in Oak Street Canal sediment are in the range of these guidelines and observations, and represent concentrations typical of relatively uncontaminated sites in urban watersheds.

At this time of printing this report, data on the 1990 collection of shiners was not available. The findings of that study will be reported in the Collingwood Harbour RAP Stage 2 document in the winter of 1991.

- Given that mussels in the harbour did not have elevated tissue residues relative to controls, the zinc elevations do not warrant extensive and highly costly remediation of the landfill site, assuming that it is the source of zinc.

- Concentrations in Oak Street Canal sediment are in the range of guidelines, standards and observations that identify the lack of observable biological effects, and are not detected in mussels.

RAP recommendations based on this study and other biological and chemical data generated from 1987 to 1991, will be included the in Stage 2 report.

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Table 1: TRACE METALS IN MUSSEL BIOMONITORS PLACED IN COLLINGWOOD HARBOUR AND HARBOUR TRIBUTARIES FOR THREE WEEKS, 1990. ALL VALUES ARE $\mu g.g^{-1}$ (PARTS PER MILLION) ON A WET WEIGHT BASIS, FOR MUSSEL TISSUE, EXCLUSIVE OF THE SHELL.

STATION DESCRIPTION		Cu	Ni	Pb	As	Cd	Se	Hg	Zn	Mn
C	BALSAM LAKE CONROL	1.35	0.50	0.80	0.74	0.54	2.14	0.01	31.5	1280
13	BLACK ASH CREEK	1.17	0.50	0.70	0.62	0.51	0.60	0.01	36.3	780
14	OAK ST. CANAL	1.73	0.43	0.63	0.77	0.58	0.77	0.01	63.0	940
15	HICKORY ST. CANAL	3.77	0.43	0.63	0.58	0.43	0.90	0.01	39.3	713
11	GOODYEAR	2.87	0.47	0.79	0.44	0.71	0.78	0.01	41.3	1503
3	STP[1] PRECHLORINATION	0.86	0.47	0.67	0.48	0.82	0.81	0.02	31.7	456
21	EAST HARBOUR	1.06	0.47	0.67	0.44	0.41	0.96	0.01	32.7	506
25	CENTRE HARBOUR	1.01	0.43	0.63	0.61	0.56	1.10	0.01	40.0	546
32	BLACK ASH CREEK MOUTH	1.33	0.47	0.67	0.74	0.83	0.90	0.02	49.7	1546

[1]sewage treatment plant, prechlorination

TABLE 2: POLYAROMATIC HYDROCARBONS[2] DETECTED IN SEDIMENT FROM COLLINGWOOD HARBOUR AND THE TRIBUTARIES WITHIN THE HARBOUR WATERSHED, 1990. VALUES ARE IN $\mu g.g^{-1}$ (parts per million) DRY WEIGHT. NO SEDIMENT WAS COLLECTED FROM THE STP PRECHLORINATION CHAMBER.

COMPOUND	DETECTION LIMIT	STATION 11 GOODYEAR OUTFALL	STATION 13 BLACK ASH CREEK	STATION 14 OAK STREET CANAL	STATION 15 HICKORY STREET CANAL	STATION 21 EAST HARBOUR	STATION 25 CENTRE HARBOUR	STATION 32 MOUTH OF BLACK ASH CREEK
ANTHRACENE	0.01	<0.01	<0.01	0.16	<0.04	<0.02	<0.01	<0.01
FLOURANTHENE	0.02	<0.02	<0.02	<0.02	0.76	0.23	<0.02	<0.02
PYRENE	0.02	<0.54	<0.06	1.40	0.80	<0.20	<0.06	<0.06
BENZO (a) ANTHRACENE	0.02	<0.02	<0.02	0.53	<0.04	<0.07	<0.02	<0.02
CHRYSENE	0.02	<0.05	<0.02	0.62	0.44	<0.10	<0.02	<0.02
BENZO (k) FLUORANTHENE	0.02	<0.02	<0.02	0.27	0.22	<0.11	<0.06	<0.06
BENZO (a) PYRENE	0.04	<0.04	<0.04	<0.38	<0.24	<0.08	<0.04	<0.04
INDENO (1,2,3-cd) YRENE	0.04	<0.04	<0.04	<0.19	<0.26	<0.05	<0.04	<0.04

^@C

[2] sediment was analyzed for over 40 additional trace organic compounds including other PAHs, organochlorine pesticides, PCBs and mirex. All values were below detection limits

FIGURE 1: STATION LOCATIONS FOR MUSSEL AND SEDIMENT COLLECTIONS, 1990.

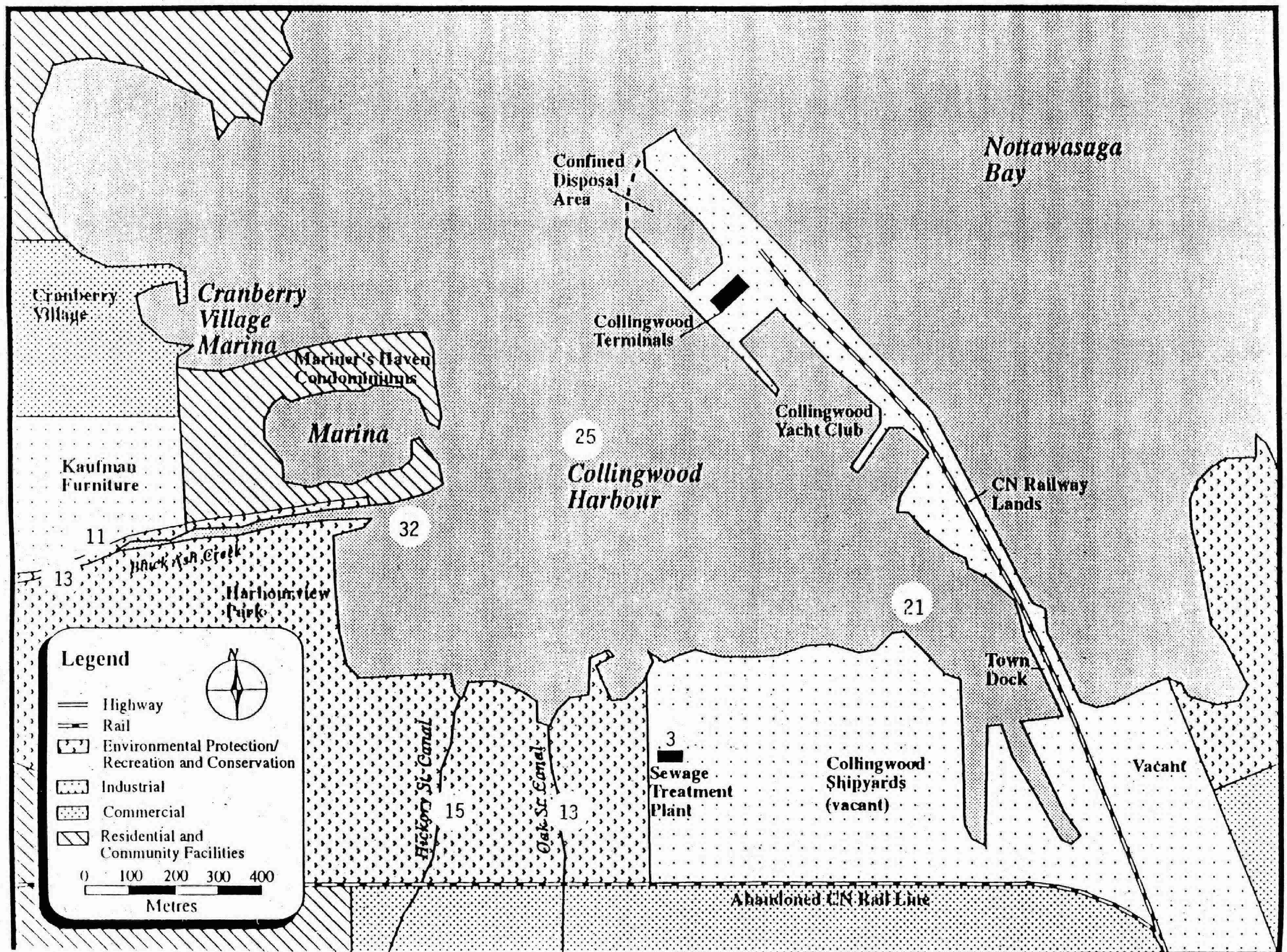
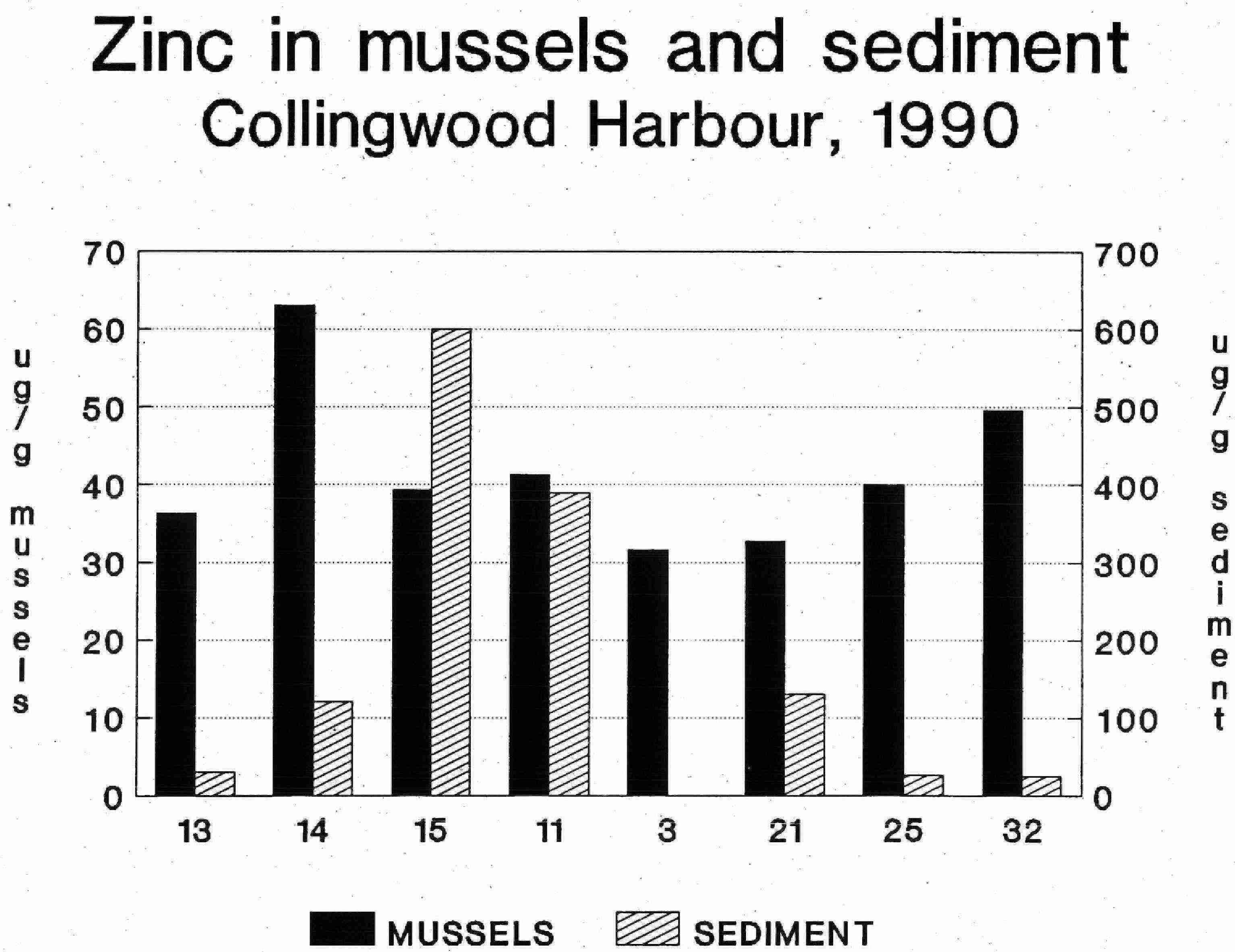


FIGURE 2



Zinc in mussels and sediment
Collingwood Harbour, 1990
70
60
50
40
30
20
10
0
ug/g mussels
700
600
500
400
300
200
100
0
ug/g sediment
13
14
15
11
3
21
25
32
MUSSELS
SEDIMENT